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(54) PROPYLENE COPOLYMER AND PROCESS FOR THE PRODUCTION THEREOF

(57) Disclosed are propylene copolymers produced by the aid of a specific metallocene catalyst system, wherein a percentage of mis-insertion in the copolymer is highly controlled and the copolymers possess heat-resisting property and a high melt strength and a low MFR and are narrow in molecular weight distribution excellent in particulate properties as well as a process for producing the copolymers possessing high steroregularity at a practical polymerization temperature. The gist of the present invention resides in production of propylene copolymers wherein copolymerization with α,ω-diene is carried out by the aid of a supported-type catalyst system comprised predominantly of the following compound (A), (B), (C) and (D) at a temperature above 45°C:

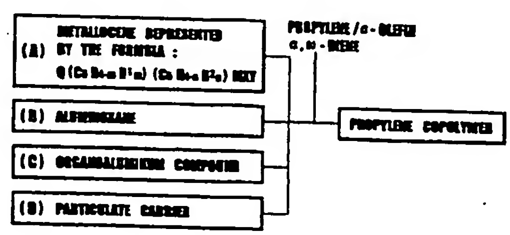
the compound (A): a specific metallocene compound represented by

$$Q\,(C_5H_{4-m}R^1{}_m)\,(C_5H_{4-n}R^2{}_n)\,MXY,$$

the compound (B): an aluminoxane,
the compound (C): an organoaluminum compound, and
th compound (D): a particulate carrier.

An important feature of the propylene copolymers of the present invention resides in the fact that the copolymers are highly stereoregular and have a ratio of a mis-inserted unit based on 2,1-insertion of propylene monomer in the total propylene insertion being defined within a specific range.

FIG. 1



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liminary polymerization with ethylene alone (Japanese Laid-open Patent Appln. No. Hei. 4-55410).

[0008] As an attempt to enhance melt tension in case of using the metallocene catalyst system, there are proposed a process wherein a catalyst comprising a silica support containing 1.0% by weight of water, a metallocene, a methylaluminoxane and triisobutylaluminum is used (Japanese laid-open Patent Appln. No. Hei. 5-140224) , a process wherein two kinds of metallocene compounds are used as catalyst component (Japanese Laid-open Patent Appln. No. Hei. 5-255436, 5-255437, and Japanese Laid-open Patent Appln. No. Hei. 6-206939) and a process wherein montmorillonite is used in the metallocene catalyst system (Japanese Laid-open Patent Appln. No. Hei. 7-188336).

[0009] In these various compositions or a process for producing thereof, however, enhancement of melt strength to a certain degree may be recognized under the measurement condition of polyolefins at 190°C, nevertheless problems still remain in enhancement of melt strength under the use condition above 200°C, remaining of odor due to a crosslinking assistant, enhancement of physical properties other than melt strength such as heat-resisting property and crystallizing temperature.

[0010] In case of using metallocene catalyst system, the processes proposed above may be effective to enhance melt tension to a certain degree under the measurement condition of polyolefin at 190°C, but are not sufficient to enhance melt tension at higher temperature, for example, under use condition above 200°C so that enhancement of melt strength is continuously desired.

[0011] In recent years, examples of copolymers of a non-conjugated diene and propylene or the like is reported which is polymerized by the aid of a metallocene catalyst, for example, in Japanese Laid-open Patent Appln. Nos. Hei. 5-222251 and Hei. 5-222121. In Examples of these publications, however, there is nowhere given the case of using metallocene catalysts. It cannot but be anticipated therefore that propylene copolymers obtained by copolymerizing propylene at a practical polymerization temperature above 45°C by the aid of a metallocene catalyst are low in stereoregularity and not satisfactory in molecular weight in addition to insufficient melt strength so that the copolymers are unable to be used practically.

[0012] In Japanese Laid-open Patent Appln. No. Hei. 7-138327, there is reported an example for copolymerization of propylene and an α,ω-diene. In this case, however, the polymerization temperature is lower than 45°C at which a practical polymerization is carried out and the molecular weight of the resultant copolymer is extremely low. What is more, since the catalyst is not carried on a support, mass production of copolymers in a practical process may be difficult.

[0013] In Japanese Laid-open Patent Appln. No. Hei. 8-92317, too, there is reported an example of copolymerzation for propylene and a polyene. However, the polymerization temperature is lower than 45°C which is a practical polymerization temperature. Further, stereoregularity of the resultant copolymer is at any rate high at a polymerization of 25°C shown in Examples but lower at a polymerization temperature above 45°C. During insertion of the total propylene, a ratio of a mis-inserted unit based on 2,1-insertion of propylene monomer is greater than 1.0% so that it cannot be said that control of high stereoregularity is made. Moreover, the catalyst system is not carried on a support so that mass production of the copolymer is impossible in a practical process.

[0014] This publication nowhere gives any description or suggestion on heat- resisting property of a copolymer of propylene or the like olefin with an α,ω-diene copolymerized by the aid of a metallocene catalyst system.

[0015] Accordingly, it is an object of the present invention to provide propylene copolymers possessing a narrow molecular weight distribution, high melt strength, heat-resisting property, a low MFR and excellent in particulate properties wherein the percentage of mis-insertion in the copolymer is highly controlled as well as a process for producing the copolymers wherein high stereoregularity is maintained even at a practical polymerization temperature.

Disclosure of the Invention

[0016] The present invention has been proposed to achieve the aforesaid object and has an important featur in copolymerization of propylene with a small amount of an α,ω-diene by the aid of a specific catalyst system.

[0017] According to the present invention, there is provided propylene copolymers comprised predominantly f a copolymer of propylene and an α,ω-diene and having a melting point of 147-160°C, a ratio of a mis-inserted unit based on 2,1-insertion of propylene monomer in the total propylene insertion being 0.05-1.0%, a content of the α,ω-diene being 0.01-2% by weight, and an Mw/Mn being 1.5-3.8.

[0018] According to the present invention, there is also provided the aforesaid propylene copolymers wherein a melting point is 152-160°C.

[0019] According to the present invention, there is further provided propylene copolymers comprised predominantly of a random copolymer of propylene and 0.1-15% by weight of ethylene and/or an α-olefin having at least 4 carbon atoms and having melting point of 100-160°C, a ratio of a mis-inserted unit based on 2,1-insertion of propylene monomer in the total propylene insertion being 0.05-1.0%, a content of an α,ω-diene being 0.01-2% by weight, and an Mw/Mn being 1.5-3.8, which has been obtained by conducting copolymerization of propylene and ethylene and/or an α-olefin having at least 4 carbon atoms.

$$Q\ (C_5H_{4-m}R^1_m)\ (C_5H_{4-n}R^2_n)\ MXY \qquad [I]$$

wherein $(C_5H_{4-m}R^1_m)$ and $(C_5H_{4-n}R^2_n)$ each stand for a substituted cyclopentadienyl group, m and n each stands for an integer of 1-3, R^1 and R^2 may be the same or different and each stands for a hydrocarbon group with 1-20 carbon atoms, a silicon-containing hydrocarbon group, with the proviso that the site and kind of R^1 and R^2 on the cyclopentadienyl rings should take a configuration where any symmetrical plane containing M is absent and that R^1 or R^2 is existent in at least one carbon atom adjacent to the carbon atom connected to Q in at least one cyclopentadienyl ring, Q stands for a bivalent hydrocarbon radical, unsubstituted silylene radical or a hydrocarbon-substituted silylene radical bridging the groups $(C_5H_{4-m}R^1_m)$ and $(C_5H_{4-n}R^2_n)$, M stands for a transition metal Ti, Zr or Hf, and X and Y may be the same or different and each stands for a hydrogen atom, a halogen atom or a hydrocarbon group,

the compound (B) being an aluminoxane,
the compound (C) being an organoaluminum compound, and
the compound (D) being a finely particulate carrier.

[0032] The propylene polymers or copolymers of the present invention obtained by the aid of the carrier type catalyst system at a temperature above 45°C are defined as given in the following factors (1)-(3) :

(1) Propylene copolymers comprised predominantly of propylene and an α,ω-diene having a melting point of 147-160°C, preferably 152-160°C, a ratio of a mis-inserted unit based on 2,1-insertion of propylene monomer in the total propylene insertion being 0.05-1.0%, a content of the α,ω-diene being 0.01-2% by weight and an Mw/Mn being 1.5-3.8.

(2) Propylene copolymers comprised predominantly of a random copolymer of propylene and 0.1-15% by weight of ethylene and/or an α-olefin having at least 4 carbon atoms and having melting point of 100-160°C, a ratio of a mis-inserted unit based on 2,1-insertion of propylene monomer in the total propylene insertion being 0.05-1.0%, a content of an α,ω-diene being 0.01-2% by weight, and an Mw/Mn being 1.5-3.8, which has been obtained by conducting copolymerization of propylene and ethylene and/or an α-olefin having at least 4 carbon atoms.

(3) Propylene-based block copolymers having a ratio of a mis-inserted unit based on 2,1-insertion of propylene monomer in the total propylene insertion being 0.05-1.0%, and a content of an α,ω-diene being 0.01-2% by weight, which are comprised of a propylene homopolymer or a propylene random copolymer containing 0.1-15% by weight of ethylene and/or an α-olefin with at least 4 carbon atoms as a first stage polymerization product, and a propylene random copolymer as a rubbery component containing 30-80% by weight of ethylene and/or an α-olefin with at least 4 carbon atoms as a successive second stage polymerization product, a proportion of the second stage polymerization product being 5-70% by weight, and an α,ω-diene having been random copolymerized at the first stage and/or the second stage polymerization.

[0033] Any of the diene compounds having a vinyl bond at at least α-position and ω-position can be used as the α,ω-diene compound used in the present invention, which may have a linear chain structure or a branched chain structure and may contain a hetero atom such as an oxygen atom, a sulfur atom or a boron atom, or a hetero atomic group. Illustrative of the α,ω-diene compound are, for example, 1,3-butadiene, 1,4-pentadiene, 1,5-hexadiene, 1,6-heptadiene, 1,7-octadiene, 1,8-nonadiene, 1,9-decadiene, 1,10-undecadiene, 1,11-dodecadiene, 1,13 tetradecadiene, and divinylbenzene. Preferable are 1,5-hexadiene, 1,7-octadiene, and 1,9-decadiene, and more preferable is 1,9-decadiene. A content of the α,ω-diene is preferably 0.01-0.1% by weight. If the content is excessive, a gel portion will be formed thus resulting in inconvenience such as recycling by re-melting being difficult.

[0034] Examples of the α-olefin utilizable for the present invention include, for example, 1-butene, 1-hexen , 2-octene, 1-decene, 4-methyl-1-pentene and styrene. Among them, 1-butene is especially preferable.

[0035] No limitation exists in the process for producing the propylene copolymers (1)-(3) of the present invention so far as the process satisfies the aforesaid factors. The propylene copolymers can, however, be produced preferably by carrying out the polymerization at a temperature above 45°C by the aid of the supported-type catalyst system.

[0036] Examples of the compound (A) in the supported-type catalyst system include any of the compounds involved in the above definition. Illustrative of the compound (A) are, for example, dimethylsilylene(2,3,5-trimethylcyclopentadienyl)(2',4',5'-trimethylcyclopentadienyl)titanium dichloride, dimethylsilylene(2,3,5-trimethylcyclopentadienyl)(2',4',5'-trimethylcyclopentadienyl)zirconium dichloride, dimethylsilylene(2,3,5-trimethylcyclopentadienyl)(2',4',5'-trimethylcyclopentadienyl)zirconium dimethyl, dimethylsilylene(2,3,5-trimethylcyclopentadienyl)(2',4',5'-trimethylcyclopentadienyl)hafnium dichloride, dimethylsilylene(2,3,5-trimethylcyclopentadienyl)(2',4',5'-trimethylcyclopentadienyl)hafnium dimethyl, dimethylsilylene-bis(2-methyl-4-phenylindenyl)zirconium dichloride, dimethylsilylene-bis(2-ethyl-4-phenylindenyl)zirconium dichloride, etc. Especially preferable is dimethylsilylene(2,3,5-trimethylcyclopentadienyl)(2',4',5'-trimethylcyclopentadienyl)zirconium dichloride.

of polymerization as scavenger.

[0044] The aforesaid supported-type catalyst component can be obtained by reacting the compound (A) with the compound (B) preferably in the presence of the compound (D). Usually, hydrocarbon-soluble m tallocene compound and aluminoxane are converted into a desired supported catalyst by allowing them to deposit on a dehydrated support.

[0045] The order of adding the metallocene compound and the aluminoxane may freely be changed. For example, the metallocene compound dissolved in an adequate hydrocarbon solvent can initially be added to the support and thereafter the aluminoxane can be added thereto. Alternatively, the aluminoxane and the metallocene compound are previously reacted together and then added to the support at the same time. It is also possible to add the aluminoxane initially to the support and then add the metallocene compound thereto. The temperature of the reaction is usually -20-100°C, preferably 0-100°C while the time required for the reaction is usually at least 0.1 minute, preferably within the range of 1-200 minutes. The supported catalyst can be used at need after preliminary polymerization with a small amount of an olefin.

[0046] Examples of an olefin used for the preliminary polymerization include ethylene, propylene, 1-butene, 1-hexene, 3-methyl-1-butene, 4-methyl-1-pentene, etc. At least two of these monomers may be copolymerized.

[0047] The supported-type catalyst thus prepared is used for polymerization or copolymerization of propylene preferably together with the organoaluminum compound (C) employed as scavenger.

[0048] A known conventional polymerization process for polymers or copolymers of propylene is applicable to a process for producing polymers or copolymers of propylene. Thus, a variety of polymerization processes can be employed such as a slurry polymerization process wherein propylene is polymerized or copolymerized in an inert solvent, for example, an aliphatic hydrocarbon such as butane, pentane, hexane, heptane or isooctane; an alicyclic hydrocarbon such as cyclopentane, cyclohexane or methylcyclohexane; an aromatic hydrocarbon such as toluene, xylene or ethylbenzene; gasoline fractions or a hydrogenated diesel oil, a bulk polymerization process wherein propylene monomer *per se* is used as a solvent, a vapor phase polymerization process wherein polymerization of propylene is carried out in a vapor phase, a solution polymerization process wherein the resultant polymer or copolymer of propyl ne formed by polymerization is liquid, or a polymerization process wherein at least two of these polymerization processes are combined.

[0049] A polymerization condition similar to that used for polymerization or copolymerization of olefins by the aid of a known Ziegler catalyst system can be adopted, which includes a polymerization temperature of 50-150°C, preferably 50-100°C, a polymerization pressure of atmospheric pressure to 7 MPa, preferably 0.2-5 MPa, and a polymerization time of usually from one minute to 20 hours. In addition, regulation of the molecular weight of the obtained polymers or copolymers of propylene is attained by suitably selecting the above polymerization condition or by introducing a molecular weight regulator such as hydrogen into the reaction system.

[0050] After completion of the copolymerization, a known conventional catalyst deactivation treatment, a step for eliminating catalyst residues, a drying step and the like after-treatment are carried out to obtain the propylene copolymer aimed at.

[0051] An intrinsic viscosity [η] of the propylene copolymer of the present invention measured in tetralin at 135°C was 0.2-10 dl/g.

[0052] In the propylene copolymer of the present invention obtained as above, a relation: $\log(MS) > -1.28\times\log(MFR) + 0.44$ exists between melt strength (MS) at 230°C and melt flow index (MFR) measured at 230°C under a load of 21.18N.

[0053] In this case, the melt strength (MS) at 230°C was measured using a melt tension tester Type 2 (manufactured by Toyo Seiki Mfg. Co. Ltd.) by heating an olefin polymer or copolymer composition at 230°C in the apparatus, extruding the molten olefin polymer or coplymer composition into the air through a nozzle having a diameter of 2.095 mm to form a strand and measuring tension (in terms of cN) of the strand of polypropylene composition taken up at a velocity of 3.14 m/min.

[0054] The propylene copolymer of the present invention has a ratio of a mis-inserted unit based on 2,1-insertion of propylene monomer in the total propylene insertion being 0.05-1.0%.

[0055] The ratio of a mis-inserted unit based on the 2,1-insertion was obtained by utilizing ^{13}C-NMR with reference to Polymer **30**, 1350 (1989).

[0056] As described in Japanese Laid-open Patent Appln. No. Hei. 7-138327 and Japanese Laid-open Pat nt Appln. No. Hei. 8-92317, a content of an α,ω-diene can be obtained by calculation utilizing ^{13}C-NMR or by calculation of a difference between the number of moles of the diene monomer supplied at the time of polymerization and th number of moles of unreacted diene monomer at the time of finishing the polymerization.

[0057] The propylene copolymers of the present invention may be incorporated with various additives such as antioxidants, UV-absorbing agents, antistatic agents, nucleating agents, lubricating agents, incombustible agents, antiblocking agents, coloring agents, inorganic or organic fillers, or with various synthetic resins so far as the object of the present invention is not damaged. Usually, the copolymers are subjected to heating followed by melt-kneading and then to cutting to form pelletized chips for manufacturing various moldings.

washed four times with 1000 ml of isopentane by decantation. The r sidue was dried *in vacuo* for 2 hours at room temperature to prepare 35 g of a supported-type catalyst.

[Production of propylene copolymer]

[0060] In a 15 liter autoclave the air in which had fully been replaced with nitrogen were placed 12 mmole of triethylaluminum, 2 g (14.5 mmole) of 1,9-decadiene and 8 liters of liquefied propylene, and the mixture was stirred for 10 minutes while elevating temperature to 50°C. A slurry of the supported-type catalyst in an amount of 2.18 g prepared as above in hexane was introduced under pressure into the autoclave while washing it with 2 liters of liquefied propylene to initiate polymerization, and the polymerization reaction was carried out for 2 hours at 50°C. The resultant powder was 1.8 kg. On analysis of the copolymer of propylene and 1,9-decadiene thus obtained revealed that a melting point was 155.8°C, a crystallizing temperature was 114.8°C, a content of 1,9-decadiene was 0.01% by weight, a ratio of a mis-inserted unit based on 2,1-insertion of propylene monomer in the total propylene insertion was 0.4%, and a melt strength was 0.6 cN. Further, an MFR was 9.5 g/10 min, an Mw/Mn was 2.5 and a bulk density was 0.43 g/ml.

[Evaluation of Heat stability]

[0061] The initial pellets have an MFR of 9.5 g/10 min while the final pellets have an MFR of 9.7 g/10 min. As a result, ΔMFR was 0.2, thus showing excellent heat stability.

⟨Example 2⟩

[Production of propylene copolymer]

[0062] In a 15 liter autoclave the air in which had fully been replaced with nitrogen were placed 12 mmole of triethylaluminum, 2 g (14.5 mmole) of 1,9-decadiene and 8 liters of liquefied propylene, and the mixture was stirred for 10 minutes while elevating temperature to 50°C. A slurry of the supported-type catalyst in an amount of 2.1 g prepared as in Example 1 in hexane was introduced under pressure into the autoclave while washing it with 2 liters of liquefied propylene to initiate polymerization, and the polymerization reaction was carried out for 2 hours at 50°C. The resultant powder was 1.9 kg. On analysis of the copolymer of propylene and 1,9-decadiene thus obtained revealed that a melting point was 156.6°C, a crystallizing temperature was 114.9°C, a content of 1,9-decadiene was 0.02% by weight, a ratio of a mis-inserted unit based on 2,1-insertion of propylene monomer in the total propylene insertion was 0.4%, and a melt strength was 7.5 cN. Further, an MFR was 1.0 g/10 min, an Mw/Mn was 2.6 and a bulk density was 0.43 g/ml.

⟨Comparative Example 1⟩

[Preparation of supported-type catalyst]

[0063] A supported-type catalyst was prepared as in Example 1 except that dimethylsilylene-bis(2-methyl-4,5-benzoindenyl)zirconium dichloride was used as metallocene in place of dimethylsilylene(2,3,5-trimethylcyclopentadienyl)(2',4',5'-trimethylcyclopentadienyl)zirconium dichloride.

[Production of propylene copolymer]

[0064] In a 15 liter autoclave the air in which has fully been replaced with nitrogen were placed 12 mmole of triethylaluminum, 2 g (14.5 mmole) of 1,9-decadiene and 8 liters of liquefied propylene, and the mixture was stirred for 10 minutes while elevating temperature to 50°C. The supported-type catalyst in an amount of 2.0 g prepared as above in a hexane slurry was introduced under pressure into the autoclave while washing it with 2 liters of liquefied propylene to initiate polymerization and the polymerization reaction was carried out for 2 hours at 50°C. The resultant powder was 2.0 kg. On analysis of the copolymer of propylene and 1,9-decadiene thus obtained revealed that a melting point was 144.2°C, a crystallizing temperature was 106.7°C, a content of 1,9-decadiene was 0.01% by weight, a ratio of a mis-inserted unit based on 2,1-insertion of propylene monomer in the total propylene insertion was 1.6%, and a melt strength was 5.9 cN. Further, an MFR was 1.1 g/10 min, an Mw/Mn was 2.7 and a bulk density was 0.40 g/ml.

ing compounds (A), (B), (C) and (D):
the compound (A) being a transition metal compound of the general formula:

$$Q\,(C_5H_{4-m}R^1{}_m)\,(C_5H_{4-n}R^2{}_n)\,MXY \qquad [I]$$

wherein $(C_5H_{4-m}R^1{}_m)$ and $(C_5H_{4-n}R^2{}_n)$ each stand for a substituted cyclopentadienyl group, m and n each stands for an integer of 1-3, R^1 and R^2 may be the same or different and each stands for a hydrocarbon group with 1-20 carbon atoms, a silicon-containing hydrocarbon group, with the proviso that the site and kind of R^1 and R^2 on the cyclopentadienyl rings should take a configuration where any symmetrical plane containing M is absent and that R^1 or R^2 is existent in at least one carbon atom adjacent to the carbon atom connected to Q in at least one cyclopentadienyl ring, Q stands for a bivalent hydrocarbon radical, unsubstituted silylene radical or a hydrocarbon-substituted silylene radical bridging the groups $(C_5H_{4-m}R^1{}_m)$ and $(C_5H_{4-n}R^2{}_n)$, M stands for a transition metal Ti, Zr or Hf, and X and Y may be the same or different and each stands for a hydrogen atom, a halogen atom or a hydrocarbon group,

the compound (B) being an aluminoxane,
the compound (C) being an organoaluminum compound, and
the compound (D) being a finely particulate carrier.

10. A process for producing propylene copolymers according to claim 9 , wherein the compound (A) is dimethylsilylene(2,3,5-trimethylcyclopentadienyl)(2',4',5'-trimethylcyclopentadienyl)zirconium dichloride or dimethylsilylene(2,3,5-trimethylcyclopentadienyl)(2',4',5'-trimethylcyclopentadienyl)hafnium dichloride.

11. A process for producing propylene copolymers according to claim 9 or 10, wherein the copolymers are produced by a vapor phase polymerization process.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP98/03945

A. CLASSIFICATION OF SUBJECT MATTER
Int.Cl⁶ C08F210/06, C08F297/08, C08F4/642

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
Int.Cl⁶ C08F10/00-10/14, 210/00-210/18, 297/06-297/08, 4/60-4/70

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP, 07-138327, A (Mitsui Toatsu Chemicals, Inc.), 30 May, 1995 (30. 05. 95), Claims ; Par. Nos. [0041] to [0047] (Family: none)	1-11
A	JP, 08-092317, A (Showa Denko K.K.), 9 April, 1996 (09. 04. 96), Claims ; Par. Nos. [0026] to [0046] (Family: none)	1-11
A	JP, 07-165814, A (Mitsui Toatsu Chemicals, Inc.), 27 June, 1995 (27. 06. 95), Claims ; Par. Nos. [0039] to [0047] (Family: none)	1-11
A	JP, 04-025514, A (Mitsui Toatsu Chemicals, Inc.), 29 January, 1992 (29. 01. 92), Claims ; page 4, lower left column, line 14 to page 5, lower left column, line 14 & EP, 476148, A & US, 5219968, A & DE, 69112322, E	1-11

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier document but published on or after the international filing date
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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
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Date of the actual completion of the international search	Date of mailing of the international search report
30 September, 1998 (30. 09. 98)	13 October, 1998 (13. 10. 98)

Name and mailing address of the ISA/	Authorized officer
Japanese Patent Office	
Facsimile No.	Telephone No.

Form PCT/ISA/210 (second sheet) (July 1992)